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(54) Title of the Invention: A method for the manufacture of copolymer polyether polyols

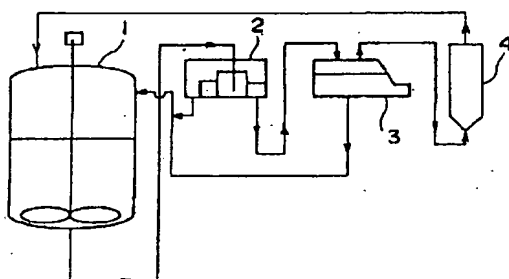
(57) Abstract

Problem

To produce in a stable manner copolymer PTMG with little variability of the copolymerization factor when manufacturing copolymer PTMG by subjecting tetrahydrofuran and diol which has from 2 to 10 carbon atoms to a copolymerization reaction.

Means of Resolution

A method for the manufacture of copolymer polyether polyols in which, when manufacturing copolymer polyether polyols from tetrahydrofuran and diols which have from 2 to 10 carbon atoms using a heteropolyacid as catalyst, some of the contents from the reaction vessel are taken out continuously and, after separating into two layers, the lower liquid layer is returned to the reaction vessel and the upper liquid layer is subjected to a process in which the water contained therein is vaporized along with tetrahydrofuran and distilled out of the system and then returned to the reaction vessel, and the liquid distillate which has been distilled out of the system is subjected to a water removal treatment and then returned to the reaction vessel.



## **Scope of the Patent Claims**

### **[Claim 1]**

A method for the manufacture of copolymer polyether polyols in which, when manufacturing copolymer polyether polyols from tetrahydrofuran and diols which have from 2 to 10 carbon atoms using a heteropolyacid as catalyst, some of the contents from the reaction vessel are taken out continuously and, after separating into two layers, the lower liquid layer is returned to the reaction vessel and the upper liquid layer is subjected to a process in which the water contained therein is vaporized along with tetrahydrofuran and distilled out of the system and then returned to the reaction vessel, and the liquid distillate which has been distilled out of the system is subjected to a water removal treatment and then returned to the reaction vessel.

## **Detailed Description of the Invention**

### **[0001]**

#### Technical Field of the Invention

The invention concerns a method for the manufacture of polyether polyols (referred to hereinafter as copolymer PTMG) which are obtained by copolymerizing tetrahydrofuran (referred to hereinafter as THF) and diols which have from 2 to 10 carbon atoms (referred to hereinafter simply as diols).

### **[0002]**

#### Prior Art

Polyoxytetramethylene glycol (referred to hereinafter as PTMG) is an industrially useful polymer which is widely used as a essential raw material for polyurethane elastomers, elastic fibers and elastic structural bodies. In recent years the copolymer ether polyols (copolymer PTMG) obtained by copolymerizing THF with diol which has from 2 to 10 carbon atoms (diol) such as neopentyl glycol (referred to hereinafter as NPG) for example have been to the fore. Said copolymer PTMG has a lower glass transition temperature than PTMG and the elastic products in which it is used as a raw material have much improved elasticity, hysteresis loss and low temperature characteristics, for example, when compared with those of materials in which PTMG has been used. For example, in the case of polyurethane elastic fibers, the conventional products in which PTMG has been used have markedly reduced instantaneous recovery below the ice point, but the elastic fibers

in which said copolymer PTMG has been used exhibit instantaneous recovery which is virtually the same as that observed at normal temperature even at temperatures as low as  $-10^{\circ}\text{C}$ .

[0003]

These improvements in characteristics are determined by copolymerization factor of the diol component in the copolymer PTMG which is being used, and the optimum copolymerization factor, and generally the copolymerization factor of the diol component (referred to hereinafter as the copolymerization factor), for copolymer PTMG materials for industrial use is selected from within the range from 5.0 and 50.0 mol%.

[0004]

The use of heteropolyacids as catalysts for the copolymerization reaction of THF and diol has been disclosed in Japanese Unexamined Patent Applications Laid Open 60-203633, 61-120830 and 61-123630. The catalytic activity of the heteropolyacids and heteropolyacid salts is disclosed in these specifications, but there is no mention at all of the setting and control of the copolymerization factor of the copolymer polyether diol which is obtained. The basis of a method with which copolymer PTMG's which have the optimum copolymerization factors for the various applications are obtained with good reproducibility and in a stable manner is the setting of the reaction conditions and operational control.

[0005]

Water is produced in the reaction when a diol is included with ether bonds in a polymer chain and it is necessary to remove the water in excess of the amount which is consumed at the polymer ends from the reaction system. Furthermore, excess water must be removed from the reaction system since the inclusion of water in an amount of not more than 15 molecules per molecule of heteropolyacid is also desirable from the viewpoint of the catalytic activity of the heteropolyacid.

[0006]

For example, there is disclosed in Japanese Unexamined Patent Application Laid Open H5-32775 a method for the manufacture of copolymer polyether polyol in which NPG and THF are reacted with a catalyst which exhibits activity in the presence of alcoholic hydroxyl groups and it is proposed that the heteropolyacids are one of the effective catalysts for this reaction, and it is also proposed that the

water which is produced by the reaction of the NPG should be removed as vapor phase water from the reaction system and that the THF which is removed at the same time should be replenished with a similar amount of fresh THF. That is to say, it is proposed in the aforementioned specification that the reaction temperature is set to the boiling temperature of the reaction liquid and the rate of replenishment of the THF is controlled in such a way as to maintain this temperature. However, with such a method it is difficult in practice to obtain in a stable manner a polymer which has the prescribed copolymerization factor. In general, the polymer concentration in the reaction system increases as the reaction proceeds and the boiling temperature of the reaction system rises. Hence, the rise in the boiling point must be suppressed by increasing the amount of THF which is used for replenishment to maintain the prescribed boiling temperature as the reaction proceeds. Consequently, the composition of the reaction liquid changes and the amount of reaction liquid in the system also increases. That is to say, the liquid surface level in the latter stages of the reaction is higher than that at the start of the reaction and there is a considerable change in the proportions of the two layers in the reaction liquid which comprises a catalyst layer and a THF layer. A small change in the conduct of the reaction, or the operational control, has a marked effect on the reaction conditions and results in a change in the polymerization factor of the copolymer polyether polyol which is obtained.

[0007]

Furthermore, the vapor phase water content of the reaction system is generally from 0.4 to 2.0 wt% and the remainder is THF and so the distillate which is removed from the reaction system has THF as the main component. The amount of liquid distillate is generally some 2.0 to 15.0 times by weight the amount of THF introduced initially, and it is necessary to replenish with more THF than this, and extra facilities are required for the management of the liquid distillate and provisions for THF replenishment. The amount of liquid distillate increases as the copolymerization factor increases and as the amount of water which is being produced increases, and large storage facilities are required for the manufacture of copolymer PTMG which has a large copolymerization factor. With the methods proposed in the aforementioned specification it is difficult to produce copolymer

PTMG which has the prescribed copolymerization factor industrially in a stable manner and cheaply.

[0008]

Problems to be Resolved by the Invention

The present invention is intended to provide a method with which copolymer PTMG which has the prescribed copolymerization factor is produced when manufacturing copolymer PTMG by reacting THF and diol using a heteropolyacid as catalyst.

[0009]

Means of Resolving These Problems

The present invention is a method for the manufacture of copolymer PTMG in which, when manufacturing copolymer PTMG from THF and diols using a heteropolyacid as catalyst, some of the contents from the reaction vessel are taken out continuously and, after separating into two layers, the lower liquid layer is returned to the reaction vessel and the upper liquid layer is subjected to a process in which the water contained therein is vaporized along with THF and distilled out of the system and then returned to the reaction vessel, and the liquid distillate which has been distilled out of the system is subjected to a water removal treatment and then returned to the reaction vessel.

[0010]

In the polymerization of THF and diol using heteropolyacid as catalyst the reaction liquid is stirred in order to provide for uniform reaction. At this time the reaction system is in the form of a liquid in which two layers, namely a THF layer and a catalyst layer, are inter-dispersed in the form of an emulsion. In the polymerization of PTMG using heteropolyacid as catalyst the polymerization reaction proceeds in the catalyst layer and, of the polymer which has been formed, that with a higher molecular weight is readily partitioned into the THF layer where further growth is stopped (Shokubai, Vol.30, No.1, 34 (1991)). It is thought that the polymerization also proceeds in the catalyst layer with the copolymers of this invention. Some of the water which is produced by the reaction of the diol is consumed at the ends of the polymer, and the remainder is partitioned between the THF layer and the catalyst layer.

[0011]

The amount of material removed from the reaction vessel should be such that from  $1/20^{\text{th}}$  to  $1/2$  the reaction liquid in the vessel is generally being replaced. If the amount removed is less than  $1/20^{\text{th}}$  then the removal from the system of the water which is being produced by the NPG reaction is retarded and the polymerization reaction takes more time. If the amount exceeds  $1/2$  then there is too much replacement of the catalyst layer in the reaction vessel and the polymerization reaction takes more time.

[0012]

The reaction liquid which is removed from the reaction vessel is transferred to a layer-separating device, such as a decanter for example, and the catalyst layer which has a higher density separates out as the lower layer and the THF layer which has a lower density separates out as the upper layer. In this invention, the lower layer liquid is returned to the reaction vessel and the upper layer liquid is transferred to an evaporator or a distillation still and the water contained in the liquid is vaporized and distilled off, together with THF, and the remaining liquid is returned to the reaction vessel, and the liquid distillate, after removal of the water from the said liquid, is returned to the reaction vessel. The reaction liquid is generally taken out of the reaction vessel continuously and so the layer-separating device and the vapor phase water and THF distillation and removal device must be of the continuous type. The distillation can be carried out at normal pressure or under reduced pressure.

[0013]

In this invention the reaction liquid which has been taken out of the reaction vessel is returned to the reaction vessel in a state where the vapor phase water of the THF layer has been removed. Hence, the catalyst composition of the reaction system does not change and the THF and diol composition in the reaction system is also held constant during the reaction in which the THF and diol units are being included in the polymer chain.



[0014]

Furthermore, in this invention the location at which the reaction is proceeding and the location at which the vapor phase water content is distilled off are separated and so the reaction temperature can be selected optionally irrespective of the distillation temperature. Specifically, it is possible to maintain a constant reaction temperature independently.

[0015]

In the present invention the THF and diol composition ratio in the reaction system is held constant and, since the temperature can also be held constant, the copolymerization factor can be determined by the conversion of the composition to polymer. That is to say, it is generally possible to produce a copolymer PTMG which has a fixed copolymerization factor by setting the amounts of each of the raw materials which are introduced to correspond with the intended copolymerization factor.

[0016]

Moreover, in this invention the THF which has been removed from the reaction system is all returned to the reaction system and so there is no need at all to supply fresh THF. Facilities for removing water from the liquid mixture of water and THF are required, but since the liquid distillate is treated continuously the water removal be achieved satisfactorily with comparatively small facilities and this is very advantageous in terms of both the installation costs of the facilities and the operating costs.

[0017]

A method in which a water-adsorbing agent such as a molecular sieve or active alumina is used, a method in which an entrainer which forms an azeotropic mixture with water of lower boiling point than the azeotropic mixture of THF and water is added and the water is removed by azeotropic distillation, a method in which high pressure distillation and low pressure distillation are combined, making use of the fact that the composition of the azeotropic mixture of THF and water changes with the pressure, an extraction and distillation method in which an appropriate solvent is added to eliminate the azeotrope of THF and water, or a membrane separation method in which use is made of a membrane through which water alone or THF alone can permeate selectively, for example, can be considered for the

method which is used to remove the water from the liquid mixture of water and THF which is used in the invention, but the abovementioned method in which an adsorbing agent such as a molecular sieve or active alumina is used and the method in which an entrainer which forms an azeotropic mixture with water of lower boiling point than the azeotropic mixture of THF and water is added and the water is removed by azeotropic distillation in particular are preferred.

[0018]

The adsorbing method in which an adsorbing agent such as a molecular sieve or active alumina is used can be a method for the adsorption and removal of water by simply bringing the liquid distillate into contact with the adsorbing agent and so it requires only the addition of small and simple facilities. Molecular sieves in particular have a great adsorbing capacity for water and they can also be regenerated easily and so they are useful for the execution of this invention.

[0019]

The abovementioned adsorbing agent may take the form of granules or lumps or a molding. A large surface area is generally required for adsorption and so the use of a material of comparatively small particle size is preferred. However, granules of diameter from about 1 to about 10 mm are more practical in consideration of the ease of handling and the pressure loss when they are used packed in an adsorbing device such as a column, tower or vessel for example.

[0020]

The usual continuous method where the liquid mixture of water and THF which is being distilled off continuously from the reaction system is sent to an adsorbing device which has been packed with molecular sieve can be used as the method for the adsorption treatment. No particular limitation is imposed upon the adsorption treatment temperature and the liquid distillate should be introduced into the adsorbing device directly at the liquid temperature.

[0021]

The adsorbing agent which has lost its adsorbing ability can be revived by circulating an inactive gas such as nitrogen or carbon dioxide gas, for example, which has been heated to a temperature of from 100 to 300°C, and the adsorbing agent can then be reused.

[0022]

Furthermore, as a result of various investigations carried out in connection with entrainers which can form a low boiling point azeotropic composition with water, the inventors have discovered that n-pentane, cyclopentane, methyl-t-butyl ether and the like form azeotropic compositions of which the boiling point is at least 10°C lower than the boiling point of the azeotropic mixture of THF and water. When these entrainers are added and the liquid is fed to a multi-stage distillation column, an azeotropic mixture of water and entrainer can be recovered from the low boiling point side and the THF can be recovered from the high boiling point side, and the recovered THF can be returned to the reaction system. The liquid of azeotropic composition on the low boiling point side separates into two layers and the entrainer can be reused, and the water should be taken out and subjected to effluent treatment etc. n-Pentane and cyclopentane have low compatibility with water and the layer separability is very good, and they are used preferably for the entrainer in this method.

[0023]

Actual examples of diols which have from 2 to 10 carbon atoms in the context of the present invention include ethylene glycol, propylene glycol, 1,3-propanediol, 1,3-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, 3-methyl-1,5-pentanediol, 1,8-octanediol, 1,10-decanediol, diethylene glycol, triethylene glycol and dipropylene glycol. Neopentyl glycol is especially desirable in terms of the low temperature characteristics, hysteresis loss and instantaneous recovery etc. of the elastomers, and in more practical terms the polyurethane fibers, in which the copolymer PTMG is used for the soft segments.

[0024]

The term heteropolyacid in this invention is a general name for the oxyacids which are formed by condensing oxyacids of elements such as P, Si, As, Ge, B, Ti, Ce, Co and the like with at least one type of oxide from among those of Mo, W and V, and the atomic ratio of the latter with respect to the former is from 2.5 to 12, and most desirably 12 or 9.

[0025]

Actual examples of these heteropolyacids include phosphomolybdic acid, phosphotungstic acid, phosphomolybdotungstic acid, phosphomolybdovanadic acid, phosphomolybdotungstovanadic acid, phosphotungstovanadic acid, phospho-

molybdoniobic acid, silicotungstic acid, silicomolybdic acid, silicomolybdotungstic acid, silicomolybdotungstovanadic acid, germaniotungstic acid, borotungstic acid, boromolybdic acid, boromolybdotungstic acid, boromolybdovanadic acid, boromolybdotungstovanadic acid, cobaltomolybdic acid, cobaltomolybdic acid, arsenomolybdic acid, arsenotungstic acid, titanomolybdic acid, ceriomolybdic acid and the like. Furthermore, no particular limitation is imposed upon the type of salt of these heteropolyacids, and they may be salts of metals of group I of the periodic table such as Li, Na, K, Rb, Cs, Cu, Ag and Au, metals group II of the periodic table such as Mg, Ca, Sr, Ba, Zn, Cd and Hg, metals of group III of the periodic table such as Sc, La, Ce, Al, Ga and In, metals of group VIII of the periodic table such as Fe, Co, Ni, Ru, Pd and Pt, and metals such as Sn, Pb, Mn and Bi, as well as ammonium salts and amine salts.

[0026]

There are no particular limitations regarding the amount of heteropolyacid used, but the smaller the amount of heteropolyacid, the lower the polymerization rate, and it is preferable to use from 0.1 to 20 times the weight of the total amount of THF and diol.

[0027]

The polymerization temperature may be from 30 to 90°C, and the time required for the reaction differs according to the copolymerization factor and the amount of catalyst, the reaction temperature and the rate at which water is being removed from the reaction system, but it is generally from about 0.5 to about 50 hours. No particular limitation is imposed upon the pressure in the reaction system and the reaction can be carried out at normal pressure, under reduced pressure or at an elevated pressure.

[0028]

The polymerization reaction proceeds in the catalyst layer on stirring the heteropolyacid with the THF and diol, and it is carried out while removing the excess water which is produced by the reaction from the separated THF layer and so there is no special need for a solvent, but a solvent which is inert in the reaction can be added, depending on the particular case.

[0029]

The polymerization reaction can be carried out as a batch reaction or as a continuous reaction.

[0030]

#### Embodiment of the Invention

The invention is described in more detail below by means of illustrative examples. However, the invention is not limited by these examples.

[0031]

#### **Example 1**

Polymerization was carried out using the polymerization reaction equipment shown in Figure 1. Thus 20.0 kg of THF and 1.7 kg of NPG were introduced into the reactor (1) which had been furnished with a stirring means, a reflux condenser and a hot-water jacket and then 13.0 kg of 12-tungsten-1-phosphoric acid dihydrate ( $\text{H}_3\text{PW}_{12}\text{O}_{40}/2\text{H}_2\text{O}$ ) were added. The hot water jacket was set to 70°C and the temperature of the reaction liquid was controlled to 65°C and the reaction was started under normal pressure by stirring. Some of the reaction liquid was removed continuously (20 liters/hour) from the bottom of the reactor starting 1 hour after starting the stirring means and this was sent to the decanter (2) and separated into two layers. The lower layer liquid was returned to the reactor and the upper layer liquid was sent to the evaporator (3) which was furnished with a liquid surface level gauge and vapor phase water was distilled off at 63°C, 440 mm Hg, together with the THF. The upper layer liquid from the decanter was fed into the evaporator continuously and so the liquid surface in the evaporator was held at a constant level, and the excess liquid was taken out of the evaporator as residual liquid and this was returned to the reactor. The liquid distillate from the evaporator was sent to the bottom of the adsorbing tower (4) (diameter 135 mm and height 950 mm) which had been packed with 10 kg of a type 3A molecular sieve and then recovered from the top of the tower and returned to the reactor. Moreover, said adsorbing tower had been pre-filled with pure THF. The water content of the THF entering the adsorbing tower was from 3,000 to 5,000 ppm, and that of the THF leaving the adsorbing column was from 100 to 200 ppm. The reaction liquid temperature in the reaction vessel varied over the range of  $65 \pm 1^\circ\text{C}$ . The reaction was stopped after 12 hours and the hot-water jacket was cooled to 45°C and the mixture was left to stand and separated into two layers, and then the upper layer liquid was collected. About

200 ml of the upper layer liquid was taken, calcium hydroxide was added and the trace amount of catalyst contained therein was precipitated out and removed by filtration. Next, the THF in the filtrate was removed by distillation and a clear viscous polymer was obtained. The polymer obtained was analyzed using  $^1\text{H-NMR}$  (400 MHz) and the results showed that it was copolymer PTMG with a copolymerization factor of 12.5 mol%.

[0032]

Repeat polymerization was carried out four times using this apparatus. The copolymerization factors of the polymers obtained were 12.5, 12.3, 12.6 and 12.4 respectively, and all of the copolymer PTMG had the same copolymerization factor within the limits of accuracy of the  $^1\text{H-NMR}$  measurements.

[0033]

### **Comparative Example**

In this example, vapor phase water was distilled off from the reactor together with THF and trapped, and the amount of THF which was being distilled off was replenished by adding fresh THF to the reactor and the reaction temperature was maintained. Thus 460 g of THF and 40 g of NPG were introduced into a reactor which had been furnished with a stirring means, a distillation means and a THF delivery means and then 300 g of 12-tungsten-1-phosphoric acid dihydrate ( $\text{H}_3\text{PW}_{12}\text{O}_{40}/2\text{H}_2\text{O}$ ) were added. The heating bath temperature was controlled in such a way that the reaction liquid temperature was set to  $70^\circ\text{C}$  and stirring was started. The reaction temperature was maintained at  $70^\circ\text{C}$  by distilling off THF which contained the vapor phase water from the reactor and supplying fresh THF to the reactor, and the reaction was carried out for 12 hours. The amount of reaction liquid when the reaction was stopped had increased by about 200 ml from that at the start of the reaction.

[0034]

The results obtained on analysis using  $^1\text{H-NMR}$  in the same way as in Example 1 showed that the copolymerization factor of the polymer was 10.1 mol%. Moreover, repeated polymerization was carried out four times. The polymerization factors of the polymers obtained were 12.0, 7.6, 9.7 and 8.9, and there was a wide spread of polymerization factors with the various reactions and the problem of reproducibility remained.

[0035]

Effect of the Invention

By using the present invention the location at which the reaction is proceeding and the location at which the vapor phase water is being distilled off are separated and it is possible to maintain a constant catalyst content, raw material composition and reaction temperature in the reaction and so it is possible to produce a copolymer polyether polyol in a stable manner with little variation in the copolymerization factor, and it is possible to produce copolymer polyether polyol which has a copolymerization factor which corresponds with its application.

**Brief Explanation of the Drawing**

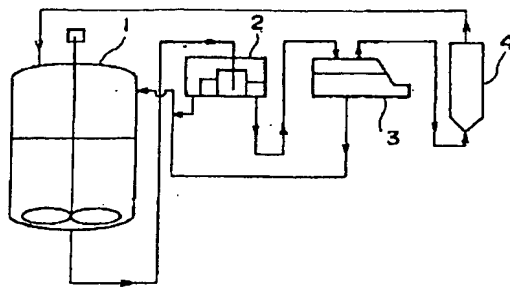
Figure 1

Figure 1 is an outline drawing of the reaction equipment used in Example 1.

Key to the Drawing

- 1: Reactor
- 2: Decanter
- 3: Evaporator
- 4: Adsorbing tower

- 15 -  
**Figure 1**





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